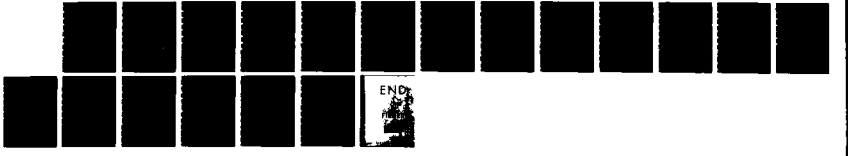
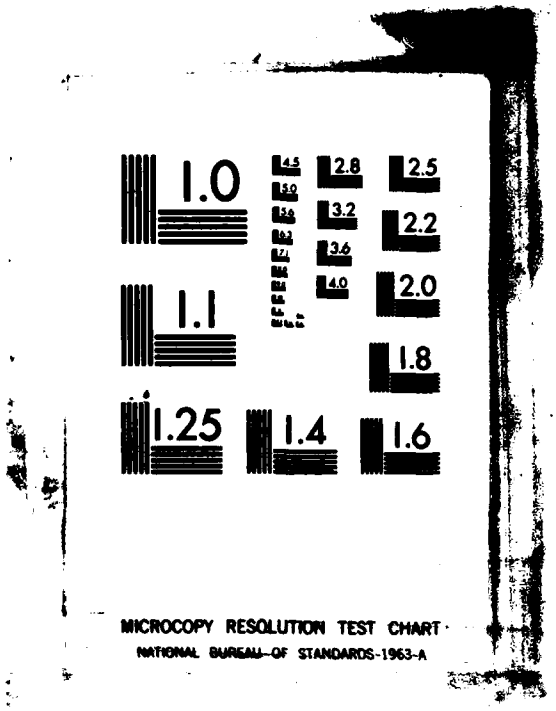
AD-A141 027 STRUCTURAL ELECTRONIC RELATIONSHIPS IN POLYMERIC SOLIDS 1/1
(U) WASHINGTON STATE UNIV PULLMAN DEPT OF CHEMISTRY
G A CROSBY FEB 83 AFOSR-TR-84-0389 AFOSR-80-0038

UNCLASSIFIED F/G 7/3 NL




1.0
1.1
1.25
1.4
1.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AFOSR-TR- 84-0389

FINAL REPORT

STRUCTURAL ELECTRONIC RELATIONSHIPS IN POLYMERIC SOLIDS

G. A. CROSBY

AFOSR-80-0038

WASHINGTON STATE UNIVERSITY
DEPARTMENT OF CHEMISTRY
PULLMAN, WA 99164-4630

OCTOBER 1, 1979 - FEBRUARY 28, 1983

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS:
2a. SECURITY CLASSIFICATION AUTHORITY:	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE:	
4. PERFORMING ORGANIZATION REPORT NUMBER(S):	5. MONITORING ORGANIZATION REPORT NUMBER(S): AFOSR-TR- 84-0389
6a. NAME OF PERFORMING ORGANIZATION: Washington State University Department of Chemistry; 6b. OFFICE SYMBOL (If applicable):	7a. NAME OF MONITORING ORGANIZATION: AFOSR/NC
6c. ADDRESS (City, State and ZIP Code): Pullman, WA 99164-4630	7b. ADDRESS (City, State and ZIP Code): Bldg 410 Bolling AFB DC 20332
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: AFOSR/NC; 8b. OFFICE SYMBOL (If applicable):	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: AFOSR-80-0038
8c. ADDRESS (City, State and ZIP Code): Bldg 410 Bolling AFB, DC 20332	10. SOURCE OF FUNDING NOS.

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
61102F	2303	A3	

11. TITLE (Include Security Classification): Structural Electronic Relationships in Polymeric Solids

12. PERSONAL AUTHOR(S): G. A. Crosby

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Final	FROM 1 Oct 79 TO 28 Feb 83	February 1983	16

16. SUPPLEMENTARY NOTATION: February 1983

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB. GR.	charge transfer	platinium(II)	ruthenium(II)
			emission	iridium(I)	osmium(II)
			luminescence	rhodium(I)	electrochemistry

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The primary objective was to quantify the excited states of metal complexes so that their ultimate roles in photophysical, photochemical, and chemical processes could be assessed. The long term goal was to arrive at a degree of sophistication such that materials with desired electrooptical properties could be designed at a molecular level and synthesized.

A comprehensive study of osmium(II) $(5d)^6$ complexes of D_3 symmetry containing N-heterocyclic ligands was completed. A new series of complexes containing $(nd)^{10}$ (n = 3,4) filled shell metal ions was synthesized and studied spectroscopically, revealing a new type of low-lying excited state. The structure of a typical example of this class of substance was determined by crystallography.

A major accomplishment was the development of a multiple-state model for the lowest excited states of $(nd)^8$ complexes. Compounds of ruthenium (II) with N-heterocyclic ligands of both D_{2d} and D_3 symmetry were also extensively investigated. The low-lying excited states of

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS ☐	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
Dr. Donald R. Ulrich	202-767-4963	AFOSR/NC

ITEM #19, ABSTRACT, CONTINUED: Measure Criterion," by L.F. Ho and the principal investigator, is a paper which largely resulted from Dr. Ho's thesis work, also supported by this grant, in part.

In addition to Dr. Ho, who is now with the University of Iowa, the principal investigator was assisted by R.G. Teglas, H.M. Baron, and R. Rebarber.

FINAL REPORT

TITLE: Structural Electronic Relationships in Polymeric Solids

INSTITUTION: Washington State University

PRINCIPAL INVESTIGATOR: G. A. Crosby

GRANT NO: AFOSR-80-0038

INCLUSIVE DATES: 1 Oct 79 - 28 Feb 83

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The primary objective was to quantify the excited states of metal complexes so that their ultimate roles in photophysical, photochemical, and chemical processes could be assessed. The long-term goal was to arrive at a degree of sophistication such that materials with desired electrooptical properties could be designed at a molecular level and synthesized.

A comprehensive study of osmium(II) $(5d)^6$ complexes of D_3 symmetry containing N-heterocyclic ligands was completed. The effect of solvents on the interactions of charge-transfer and ligand-field excited states was also quantified. A new series of complexes containing $(nd)^{10}$ (n = 3,4) filled-shell metal ions was synthesized and studied spectroscopically revealing a new type of low-lying excited state. The structure of a typical example of this class of substances was determined by crystallography.

A major accomplishment was the development of a multiple-state model for the lowest excited states of $(nd)^8$ complexes, which was applied to several examples of rhodium(I) and iridium(I) complexes. Compounds of ruthenium(II) with N-heterocyclic tridentate ligands and D_{2d} symmetry were also quantified spectroscopically. The visible bands and the lowest emitting levels were assigned group-theoretically via polarization ratio spectroscopy. Trigonal (D_3) complexes of ruthenium(II) were extensively investigated by luminescence measurements. Dimeric complexes

containing two coordinated metal ions of $(nd)^8$ electronic structure [Pt(II)-Pt(II), Rh(I)-Rh(I)] were synthesized and investigated spectroscopically. Decay constants and splittings of the lowest levels were determined and a molecular orbital model to rationalize the lowest excited states was developed. The identity of the electron acceptor orbital in charge-transfer excited configurations of iridium(I) complexes containing N-heterocycles with the electron acceptor orbital involved in electrochemical reduction of the molecules was established, thus linking electronic spectroscopy with electrochemistry. Finally, a model for predicting the intensities of charge-transfer excited states in symmetrical complexes was developed mathematically and applied to the lowest states of copper(I) and ruthenium(II) D_{2d} complexes. The natures of the lowest excited states of these species were also quantified spectroscopically by luminescence decay time and polarization ratio spectroscopy.

OBJECTIVES

The primary immediate objective of the research was to quantify the excited states of metal complexes so that their ultimate roles in photophysical, photochemical, and chemical processes could be assessed. The proposed emphasis of the studies was on charge-transfer-to-metal (CTTM) excited states, particularly of those complexes that display both photochemical and thermal stability and have low-lying CTTM excited states that are accessible with visible radiation. A second, long-term objective was to arrive at a degree of sophistication of the models for excited states such that new materials, particularly polymeric solids with desired electrooptical properties, could be designed from a molecular point of view using structural electronic relationships.

Excited States of Osmium(II) Complexes

Comprehensive spectroscopic investigations of the lowest charge-transfer excited states of osmium(II) complexes were completed. [See publications 49,50.]

The lowest electronic states were definitively assigned to charge-transfer-to-metal (CTTM) states; the radiative and radiationless rate constants of the three lowest components of the emitting manifolds were determined and the energy separations of the electronic levels were quantified. The states were assigned by the use of a model for $(nd)^6$ excited states developed in this laboratory [40].

Solvent Perturbations of Iridium(III) Excited States

Extensive solvent effect studies on iridium(III) complexes delineated the role of solvents in modulating ligand $\pi\pi^*$-charge transfer $d\pi^*$ interactions [51]. A new model compound $[IrCl_2(4,4'\text{-}Me_2bpy)_2Cl]$ was proposed as a standard for charge-transfer emissions.

Spectroscopic Study of $(nd)^{10}$ Complexes

An investigation of a number of zinc(II) and cadmium(II) complexes containing aromatic thiol and N-heterocyclic ligands was carried out. A crystallographic structural determination of a typical molecule was completed [52]. The molecules are pseudotetrahedral. The lowest excited electronic states of these systems were elucidated by means of luminescence decay time measurements and absorption spectroscopy. A low-lying excited state inferred to arise from an unusual interligand transmetallic charge transfer electronic configuration was discovered [67,68,69].

Excited States of $(nd)^8$ Monomeric Complexes of Rhodium(I) and Iridium(I)

The lowest excited states of several complexes of iridium(I) and rhodium(I) containing metal-phosphorous and/or metal arsenic bonds were quantified by luminescence spectroscopy [53,61]. Particularly important was the confirmation that the multiple-state phenomenological model developed for ruthenium(II) and osmium(II) $(nd)^6$ charge-transfer excited state manifolds was applicable to $(nd)^8$ charge-transfer and ligand-field excited terms as well [38,39,40,49,50]. Term splittings and decay constants for Ir(I) and Rh(I) species were determined for a series of molecules. The role of spin-orbit coupling in defining the properties

of the low-lying excited state manifolds was defined and related to the bonding in the molecules.

Symmetry Assignments of the Charge-Transfer Excited States of D_{2d} Complexes of Ruthenium(II) with Bis(tripyridine) Ligands

Several ruthenium(II) species were synthesized and investigated spectroscopically. The low-lying excited states were unequivocally assigned to charge-transfer configurations [54,62]. Polarization measurements of the spectra revealed fundamental changes in the sign of the polarization ratio as the temperature was lowered from 50 to 5 K [57]. These results indicate that D_{2d} symmetry is retained in the excited state, a situation that contrasts fundamentally with the behavior of ruthenium(II) D_{3d} complexes possessing analogous ligands [66]. One of the D_{2d} systems is of potential interest to photochemists for solar energy research [54] since the complex has an excited state lifetime in fluid solution sufficiently long to allow both energy transfer and redox chemistry to occur from the excited state manifold before radiationless degradation occurs.

Electronic Structures of Platinum(II) and Rhodium(I) Dimeric Complexes

A thorough study of the excited states of a recently synthesized Pt(II)-Pt(II) octaphosphite ion was completed [56]. By means of luminescence measurements supplemented by Franck-Condon analysis of the emission band(s), it was determined that the excitation energy was essentially confined between the Pt-Pt centers, that the spin-orbit coupling within the lowest triplet term vanished to first order, and that the Pt-Pt bond increased in bond strength upon excitation. Analogous results were obtained for a series of bridged rhodium(I) dimers that are isoelectronic with platinum(II) in the d-shell [58]. Since platinum(II) species emits light in fluid solution, the lifetime of the lowest state is long enough to allow photochemistry to compete with thermal degradation of the excitation energy. A simple molecular orbital scheme was developed to rationalize the existence and properties of the lowest excited states of these unusual substances.

Investigation of N-Heterocyclic Complexes of Rhodium(I) and Iridium(I)

A systematic study of a series of rhodium(I) and iridium(I) complexes was carried out to relate the optical properties to the redox behaviors of the materials. Luminescence measurements revealed that the lowest triplet term of all the complexes was derived from a charge-transfer configuration where the electron is promoted from the metal ion to a π^* orbital on the N-heterocyclic ligand [59]. Concomitant electrochemical measurements showed the acceptor orbital in the reduced species to be the same as the acceptor orbital for the electron in the excited charge-transfer configuration. This study uniquely related the detailed knowledge of the excited configuration obtained by low-temperature spectroscopic measurements to the electrochemical results derived from solution measurements at ambient temperatures. Achieving such correspondence was one of the principal goals of the program.

Analysis of the Excited States of Copper(I) Complexes Containing N-Heterocyclic Ligands

Several bis bidentate complexes of copper(I) were synthesized and subjected to a thorough spectroscopic study by both absorption and luminescence techniques. The results showed that the visible absorption spectra of these (almost) D_{2d} species are charge-transfer in nature [62]. It was also determined that the lowest triplet term is ^3E (in D_{2d}) and subject to strong spin-orbit coupling [65]. An intensity model for predicting the oscillator strengths of charge-transfer transitions in symmetrical complexes (which is applicable to charge-transfer transitions of broad classes of complexes) was developed [63] and employed to rationalize the spectra of Cu(I) complexes of near D_{2d} symmetry [64]. These copper(I) complexes also display the requisite features needed for serving as energy donors, reductants, or oxidants in fluid solution after the absorption of visible radiation.

Magnetic Field Effects on Excited States

A magnetic field effect on the emission spectra of a bis iridium(I) complex containing diphenylphosphinoethylene ligands has been discovered. Spectral shifts of 300 cm^{-1} have been recorded in fields ranging up to 52 kGauss. A model for the effect, which involves the relaxation of optical selection rules via the mixing of allowed character into forbidden states through field-dependent off-diagonal matrix elements has been developed [AFOSR 80-0038 Progress Report #4].

Structural Electronic Relationships

Substantial progress was made toward the goal of modeling excited charge-transfer states of $(nd)^6$, $(nd)^8$, and $(nd)^{10}$ complexes where spin-orbit coupling plays a major role in determining the properties of the levels. The relationship of structure and bonding to photochemical reactivity was also semiquantitatively defined. Of major importance was the development of a multiple-state model and applicable data reduction methods that allow the extraction of excited state level properties and splittings from the analysis of the temperature dependence of decay times when direct spectroscopic observation is precluded. Finally, a substantial number of new luminescent substances was synthesized and shown to possess the requisite properties for displaying interesting and potentially important photochemical reactivity.

PUBLICATIONS

Cumulative List of AFOSR-supported Publications

* Reprints of article and DD 1473 sent to AFOSR.

* 1. G. A. Crosby, W. G. Perkins, and D. M. Klassen, "Luminescence From Transition-Metal Complexes: Tris(2,2'-bipyridine)- and Tris(1,10-phenanthroline)ruthenium(II)," Journal of Chemical Physics 43, 1498 (1965).

* 2. G. A. Crosby, "Luminescent Organic Complexes of the Rare Earths," a review, Molecular Crystals 1, 37 (1966).

* 3. G. A. Crosby, D. M. Klassen, and S. L. Sabath, "Intramolecular Energy Transfer in Osmium(II) Complexes," Molecular Crystals 1, 453 (1966).

* 4. G. A. Crosby, "Optical Excitation of Transition-Metal Ions Via Intramolecular Energy Transfer," Journal de Chimie Physique 64, 160 (1967).

* 5. D. M. Klassen and G. A. Crosby, "Reassignment of the Luminescence From Ruthenium(II) Complexes," Chemical Physics Letters 1, 127 (1967).

* 6. D. M. Klassen and G. A. Crosby, "Ligand-Field Transitions in Tertiary Phosphine and Arsine Complexes of Ruthenium(II) and Osmium(II)," Journal of Molecular Spectroscopy 25, 398 (1968).

* 7. D. M. Klassen and G. A. Crosby, "Spectroscopic Studies of Ruthenium(II) Complexes. Assignment of the Luminescence," Journal of Chemical Physics 48, 1853 (1968).

8. G. A. Crosby and R. D. Caton, "Review of Fluorescence and Phosphorescence Analysis: Principles and Applications edited by D. M. Hercules," Journal of the Franklin Institute 286, 93 (1968).

* 9. J. N. Demas and G. A. Crosby, "On the Multiplicity of the Emitting State of Ruthenium(II) Complexes," Journal of Molecular Spectroscopy 26, 72 (1968).

* 10. G. A. Crosby and D. H. W. Carstens, "Luminescence From Rhodium(III) and Iridium(III) Complexes," Molecular Luminescence, ed. E. C. Lim, W. A. Benjamin, 1969, p. 309.

* 11. J. N. Demas, T. F. Turner, and G. A. Crosby, "Preparation and Thin-Layer Chromatography of cis-Dicyanobis(2,2'-bipyridine)ruthenium(II)," Inorganic Chemistry 8, 674 (1969).

* 12. D. H. W. Carstens and G. A. Crosby, "Luminescence From Complexes of Rhodium(III)," Journal of Molecular Spectroscopy 34, 113 (1970).

* 13. R. W. Harrigan and G. A. Crosby, "Temperature Dependence of the Luminescence of Tb^{3+} Complexes," Journal of Chemical Physics 52, 4912 (1970).

* 14. G. A. Crosby and B. Pankuch, "Cryostat for Spectroscopic Measurements of Solutions and Rigid Glasses," Chemical Instrumentation 2, 329 (1970).

PUBLICATIONS - continued

* 15. J. N. Demas and G. A. Crosby, "Photoluminescence Decay Curves: An Analysis of the Effects of Flash Duration and Linear Instrumental Distortions," Analytical Chemistry 42, 1010 (1970).

* 16. R. W. Harrigan and G. A. Crosby, "Variable Temperature Sample Mount for Luminescent Powders," Spectrochimica Acta 26A, 2225 (1970).

* 17. J. N. Demas and G. A. Crosby, "Quantum Efficiencies of Transition-Metal Complexes. I. d-d Luminescence," Journal of the American Chemical Society 92, 7262 (1970).

* 18. G. A. Crosby, R. J. Watts, and D. H. W. Carstens, "Inversion of Excited States of Transition-Metal Complexes," Science 170, 1195 (1970).

* 19. R. J. Watts, R. W. Harrigan, and G. A. Crosby, "Temperature and Magnetic Field Effects on the Luminescence Lifetimes of Complexes of Ruthenium(II) and Iridium(III)," Chemical Physics Letters 8, 49 (1971).

* 20. T. R. Thomas and G. A. Crosby, "Luminescence From Rhodium(III) Ammine Complexes," Journal of Molecular Spectroscopy 38, 118 (1971).

* 21. J. N. Demas and G. A. Crosby, "The Measurement of Photoluminescence Quantum Yields. A Review," Journal of Physical Chemistry 75, 991 (1971).

* 22. J. N. Demas and G. A. Crosby, "Quantum Efficiencies of Transition-Metal Complexes. II. Charge-Transfer Luminescence," Journal of the American Chemical Society 93, 2841 (1971).

* 23. R. J. Watts and G. A. Crosby, "Spectroscopic Characterization of Complexes of Ruthenium(II) and Iridium(III) with 4,4'-Diphenyl-2,2'-bipyridine and 4,7-Diphenyl-1,10-phenanthroline," Journal of the American Chemical Society 93, 3184 (1971).

24. G. A. Crosby, R. W. Harrigan, and R. J. Watts, "Optical Measurement of Temperature," Patent Applied For.

* 25. G. A. Crosby, R. J. Watts, and S. J. Westlake, "Phosphorescence of Acetylacetonates of Trivalent Metals," Journal of Chemical Physics 55, 4663 (1971).

* 26. R. J. Watts and G. A. Crosby, "Quantum Efficiencies of Transition-Metal Complexes. III. The Effect of Ligand Substituents on Radiative and Radiationless Processes," Journal of the American Chemical Society 94, 2606 (1972).

* 27. R. J. Watts and G. A. Crosby, "A Comparison of $n\pi^*$-$\pi\pi^*$ Interactions in Aromatics with $d\pi^*$-$\pi\pi^*$ Interactions in Iridium(III) Complexes," Chemical Physics Letters 13, 619 (1972).

PUBLICATIONS - continued

* 28. R. J. Watts, G. A. Crosby, and J. L. Sansregret, "Excited States of Transition-Metal Complexes. A Spectroscopic Measurement of $d\pi^*$-$\pi\pi^*$ Interactions in Iridium(III) Complexes," Inorganic Chemistry 11, 1474 (1972).

29. G. A. Crosby, J. N. Demas, and J. B. Callis, "Absolute Quantum Efficiencies," a review

* a. Journal of Research, National Bureau of Standards, 76A, 561 (1972)

b. and in the Proceedings of the Conference on Accuracy in Spectrophotometry and Luminescence Measurements, NBS, Gaithersburg, Maryland, March 22-24, 1972. (NBS Special Publication 378, May 1973, p. 151).

* 30. T. R. Thomas, R. J. Watts, and G. A. Crosby, "Radiative and Radiationless Decay Processes in Rhodium(III) Ammine Complexes," Journal of Chemical Physics, 59, 2123 (1973).

* 31. R. W. Harrigan, G. D. Hager, and G. A. Crosby, "Evidence for Multiple-State Emission from Ruthenium(II) Complexes," Chemical Physics Letters, 21, 487 (1973).

* 32. R. W. Harrigan and G. A. Crosby, "Symmetry Assignments of the Lowest CT Excited States of Ruthenium(II) Complexes via a Proposed Electronic Coupling Model," Journal of Chemical Physics, 59, 3468 (1973).

* 33. G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., "On the Appropriateness of Assigning Spin Labels to Excited States of Inorganic Complexes," Journal of the American Chemical Society, 96, 629 (1974).

* 34. J. L. Sansregret and G. A. Crosby, "Molecular Sieves as Media for Growing Crystals," Journal of Crystal Growth, 21, 313 (1974).

* 35. K. W. Hipps and G. A. Crosby, "Geometrical Distortion and Spin-Orbit Splitting in Excited Transition-Metal Complexes," Inorganic Chemistry, 13, 1543 (1974).

* 36. D. C. Baker and G. A. Crosby, "Spectroscopic and Magnetic Evidence for Multiple-State Emission from Tris(2,2'-bipyridine)ruthenium(II) Sulfate," Chemical Physics, 4, 428 (1974).

* 37. G. A. Crosby, G. D. Hager, K. W. Hipps, and M. L. Stone, "Investigation of the Temperature Dependence of Ruthenocene Photoluminescence," Chemical Physics Letters, 28, 497 (1974).

* 38. G. D. Hager and G. A. Crosby, "Charge-Transfer Excited States of Ruthenium(II) Complexes. I. Quantum Yield and Decay Measurements," Journal of the American Chemical Society, 97, 7031 (1975).

* 39. G. D. Hager, R. J. Watts, G. A. Crosby, "Charge-Transfer Excited States of Ruthenium(II) Complexes. II. Relationship of Level Parameters to Molecular Structure," Journal of the American Chemical Society, 97, 7037 (1975).

PUBLICATIONS - continued

* 40. K.W. Hipps and G.A. Crosby, "Charge-Transfer Excited States of Ruthenium(II) Complexes. III. An Electron-Ion Coupling Model for d * Configurations", Journal of the American Chemical Society 97 7042-7048 (1975)

* 41. G. A. Crosby, "Spectroscopic Investigations of Excited States of Transition-Metal Complexes", Accounts of Chemical Research 8, 231-238 (1975).

* 42. G. A. Crosby, "Luminescence as a Probe of Excited State Properties", Advances in Chemistry Series, No. 150, R. B. King, Ed. (Proceedings of the Symposium on Inorganic Compounds with Unusual Properties, University of Georgia, Jan. 1975), American Chemical Society, Washington, D. C., 1976, Chap 13, pp 149-159.

* 43. G.A. Crosby and W. H. Elfring, Jr., "Excited States of Mixed Ligand Chelates of Ruthenium(II) and Rhodium(III)" (Plenary address, Michael Kasha Symposium on Electronic Proceeese and Energy Transfer in Organic, Inorganic, and Biological Systems, Florida State University, Jan 1976), Journal of Physical Chemistry 80, 2206-2211 (1976).

* 44. K.W. Hipps, G. A. Merrell, G.A. Crosby, "Geometrical Distortion of the Excited States of d^6 Transition Metal COmplexes: Systems of O and D_4 Symmetry" (Proceedings of the Michal Kasha Symposium), Journal of Physical Chemistry 80, 2232-2239 (1976).

* 45. K. W. Hipps, "The Molecular Theory of Polarized Emission : Linear, Circular, and Magnetically Induced Circular Polarization of Emission", Chemical Physics 23, 451-463 (1977).

* 46. K.W. Hipps and G.A. Crosby, "Magnetically Induced Circular Polarization of Emission: Application to Inorganic Complexes", Proceedings of the 21st Annual Symposium of the Society of Photo-optical and Instrumentation
a. Engineers, San Diego, August 22-27, 1977. SPIE 112, 132-137 (1977) and
b. in Optical Engineering 17, 176-179 (1978).

* 47. D.C. Baker, K.W. Hipps, G.A. Crosby, "Infrared-Optical Double Resonance and Thermal Modulation Spectroscopy of the Tris(2,2'-bipyridine)-Ruthenium(II) Cation", Chemical Physics Letters 53, 333-336 (1978).

* 48. K.W. Hipps and G.A. Crosby, "Applications of the Photoelastic Modulator to Polarization Spectroscopy", Journal of Physical Chemistry 83, 555-562 (1979).

* 49. B.J. Pankuch, D.E. Lacky, G.A. Crosby, "Charge-Transfer Excited States of Osmium(II) Complexes: I. Assignment of the Visible Absorption Bands", Journal of Physical Chemistry 84, 2061-2067 (1980).

* 50. D.E. Lacky, B.J. Pankuch, G.A. Crosby, "Charge-Transfer Excited States of Osmium(II) Complexes: II. Quantum Yield and Decay Time Measurements", Journal of Physical Chemistry 84, 2068-2074 (1980).

PUBLICATIONS - continued

* 51. T.L. Cremers and G.A. Crosby, "Solvent Effects on the Luminescing Excited States of Iridium(III) Complexes", Chemical Physics Letters 73, 541-544 (1980).

* 52. T.L. Cremers, D.R. Bloomquist, R.D. Willett, G.A. Crosby, "Structure of Bis(4-tolluenethiolato-1,10-phenanthroline)zinc(II)", Acta Crystallographica B36, 3097-3099 (1980).

* 53. W. A. Fordyce, H. Rau, M. L. Stone, G. A. Crosby, "Multiple State Emission from Rhodium(I) and Iridium(I) Complexes", Chemical Physics Letters 77, 405-408 (1981).

* 54. M. L. Stone and G. A. Crosby, "Charge-Transfer Luminescence from Ruthenium(II) Complexes Containing Tridentate Ligands", Chemical Physics Letters 79, 169-173 (1981).

* 55. W.H. Elfring, Jr. and G.A. Crosby, "Excited States of Mixed-Ligand Chelates of Ruthenium(II): Quantum Yield and Decay Time Measurements", Journal of the American Chemical Society 103, 2683-2687 (1981).

* 56. W. A. Fordyce, J. G. Brummer, G. A. Crosby, "Electronic Spectroscopy of a Diplatinum(II) Octaphosphite Complex", Journal of the American Chemical Society 103, 7061-7064 (1981).

* 57. S. F. Agnew, M. L. Stone, G. A. Crosby, "Emission Spectra, Decay Times, and Polarization Ratios of Ruthenium(II) Complexes Containing Tridentate Ligands", Chemical Physical Letters 85, 57-60 (1982).

* 58. W. A. Fordyce and G. A. Crosby, "Electronic Spectroscopy of Diphosphine and Diarsine Bridged Rhodium(I) Dimers", Journal of the American Chemical Society 104, 985-988 (1982).

* 59. W. A. Fordyce and G. A. Crosby, "Electronic Spectroscopy of N-Heterocyclic Complexes of Rhodium(I) and Iridium(I)", Inorganic Chemistry 21, 1023-1026 (1982).

* 60. W. A. Fordyce, K. H. Pool, G. A. Crosby, "Electrochemistry of N-Heterocyclic Complexes of Rhodium(I) and Iridium(I)", Inorganic Chemistry 21, 1027-1030 (1982).

* 61. W. A. Fordyce and G. A. Crosby, "Electronic Spectroscopy of Diphosphine and Diarsine Complexes of Rhodium(I) and Iridium(I)", Inorganic Chemistry 21, 1455-1461 (1982).

* 62. G. A. Crosby, "Structure, Bonding, and Excited States of Coordination Complexes", Journal of Chemical Education 60, 791-796 (1983).

PUBLICATIONS - continued

63. W. L. Parker and G. A. Crosby, "An Intensity Model for Charge-transfer-to Metal Transitions in Complexes" (to be submitted to J. Phys. Chem.)

A generalized model of the intensity of electronic charge transfer transitions has been developed. This model encompasses both transition metal and simple organic donor acceptor complexes. The fundamental tenet of the argument is that local dipole moment terms dominate the transition moment expression. This assumption was made in analogy with the generally accepted dominance of the static dipole moment terms in the transition moment expressions for organic donor acceptor complexes. General criteria for the presence of intense charge transfer absoprtion bands have been formulated within this context. The proposed model provides these criteria without recourse to detailed calculation. If the local dipole moment terms are not dominant, only direct computation of transition moments will be able to predict the presence of intense charge transfer bands. Complex symmetry was seen to be important in recounting the number and relative intensities of the absorption bands.

64. W. L. Parker and G. A. Crosby, "Application of a Charge-Transfer Intensity Model to the Visible Absorption Bands of Ruthenium(II) and Copper (I) Complexes of D_{2d} Symmetry" (to be submitted to J. Phys. Chem.)

A newly formulated charge-transfer intensity model has been applied to rationalize the observed absorption spectra of some ruthenium(II) and copper(I) complexes containing π-conjugated ligands and exhibiting D_{2d} symmetry. The principal absorption band occurring in the visible region of the spectrum in each case is assigned to a z-polarized transition related to an e(metal) $\rightarrow$ e(ligand) one-electron promotion.

65. W. L. Parker and G. A. Crosby, "Assignment of the Lowest Emitting Term in Ruthenium(II) and Copper(I) Complexes of D_{2d} Symmetry" (to be submitted to J. Phys. Chem.)

The lowest emitting term of several bis(tripyridine) complexes of ruthenium(II) has been assigned to $^3B_1$ symmetry in D_{2d}. For copper(I) complexes of analogous structure and chemical composition the lowest term is assigned to ^3E. The experimental basis and electronic orbital properties dictating these assignments is discussed in terms of the relative dispositions of metal d-orbitals in the d^6 and d^{10} cases.

66. S. F. Agnew and G. A. Crosby, "Evidence for Excited State Jahn-Teller Distortion in Trigonal Ruthenium(II) Chelates" (in preparation)

An extensive investigation via polarization ratio spectroscopy of mono, bis, and tris(2,2'-bipyridine) and -(1,10-phenanthroline) complexes of ruthenium(II) [and osmium(II)] has been completed. The conclusion is that significant distortion away from D_3 symmetry occurs only in the excited state and Jahn-Teller distortion lowers the spin-orbit coupling energy by an order of magnitude from the value expected in D_3.

PUBLICATIONS - continued

67. K. A. Truesdell, R. G. Highland, G. A. Crosby, "Spin-Orbit Coupling in Zinc(II) and Cadmium(II) Complexes" (in preparation)

Studies of relative phosphorescence to fluorescence yields (ϕ_p/ϕ_f) of a series of complexes of the formula $M(N\text{-}N)X_2$ have been carried out at 77 K. The results show a clear dependence of ϕ_p/ϕ_f on the spin-orbit coupling parameters of both the metal ions and the coordinated halides. The relevance of this information to radiationless transition probabilities in non-halogen containing complexes exhibiting interligand transmetallic charge-transfer excited states is discussed.

68. K. A. Truesdell and G. A. Crosby, "Excited States of $(nd)^{10}$ Complexes: Location of Low-lying Charge-Transfer States" (in preparation)

Room temperature absorption and low temperature emission spectra (77 K) of a series of zinc(II) and cadmium(II) complexes of the type $M(SL)_2(s\text{-}N\text{-}N)$ [M = Zn(II), Cd(II); SL = substituted benzene thiol; s-N-N = substituted bipyridine or 1,10-phenanthroline] reveal the existence of low-energy electronic transitions in the near uv, visible, and near ir regions of the spectrum. The states can be tuned in frequency by judicious changes of the ligands. The transitions seen in absorption are broad and weak, indicating large changes in geometry upon excitation. The states are tentatively assigned to interligand transmetallic charge-transfer configurations.

69. K. A. Truesdell, R.G. Highland, G.A. Crosby, "Excited States of $(nd)^{10}$ Complexes: Low-temperature Investigation of Low-lying Charge-Transfer States" (in preparation)

A spectroscopic study of several complexes of zinc(II) containing both benzene thiol and 1,10-phenanthroline ligands has confirmed the existence of low-lying charge-transfer states that are characteristic of the system and not of the individual ligands. Spectra taken with box-car averaging techniques reveal the existence of several low-lying excited states of both individual ligand type and interligand charge transfer characteristics. A model for the lowest charge-transfer states in $(nd)^{10}$ systems of this type is proposed.

Dissertations/Thesis Completed During Grant Tenure

W. A. Fordyce, "Spectroscopic and Electrochemical Investigations of Rhodium(I) and Iridium(I) Complexes", Ph.D., 1981.

S. F. A[illegible]ew, "The Polarization Ratio Spectroscopy of Ruthenium(II) Polypyridyl Che[illegible]", Ph.D., 1981.

W. L. [illegible]rke[illegible] 'Development of a Chrage Transfer Intensity Model and Its Application to the Electronic Spectra of D_{2d} Complexes of Ruthenium(II) and Copper(I)", Ph.D., 19[illegible].

A. D. Crosby, "Synthesis and Spectroscopic Properties of Some Novel Zinc(II) and Cadmium(II) Complexes", M.S. officially received June 1983.

INVITED TALKS AND LECTURES (Reports of AFOSR-related research) June 1980 -

Dates of presentations are listed chronologically under each title

"Determination of Excited State Properties", Tutorial on Photochemistry, Northwest Regional American Chemical Society Meeting, Salt Lake City, UT, June 1980.

"Electronic Structures and Properties of Transition-Metal Complexes", Five-lecture series, University of Wyoming, Laramie, WY, July 1980.

"Probing the Electronic Structures of Transition-Metal Complexes by Luminescence Techniques", Richland Section, American Chemical Society, Richland, WA, Sept 1980.

"Properties of Electronic Excited States of Rhodium(I), Iridium(I), and Platinum(II) Complexes"

Physical Chemistry Seminar, Florida State University, Tallahassee, FL, Apr 1981.
Division of Sciences Seminar, University of Puerto Rico, San Juan, PR, Apr 1981.
Department of Chemistry, Western Washington University, Bellingham, WA, May 1981.
Georgia Pacific Corporation, Bellingham, WA, May 1981.
Chemistry Department, Hope College, Holland, MI, Feb 1982
Department of Chemistry Seminar, University of Hawaii, Honolulu, Nov 1982
Chemistry Department Seminar, New Mexico State University, Las Cruces, Nov 1982

"Cyclovoltammetric and Spectroscopic Investigations of Transition Metal Complexes", Inorganic Seminar, Florida State University, Tallahassee, FL, Apr 1981.

"Spectroscopic and Electrochemical Investigations of Organotransition Metal Catalysts", Center for Fundamental Energy Research Annual Review, Washington State University, May 1981.

"Light As a Research Tool: Luminescence and Molecular Design", 48th Washington State University Distinguished Faculty Address, Oct 1981.

"Photophysics and Photochemistry of Dimeric Platinum(II) and Rhodium(I) Complexes"

University of Oregon, Nov 1981.
Oregon State University, Nov 1981.
University of Washington, Nov 1981.
Western Washington University, Dec 1981
Oklahoma State University, Apr 1982
University of Arizona, May 1982
University of Michigan, Oct 1982
Purdue University, Apr 1983

INVITED TALKS AND LECTURES - contd

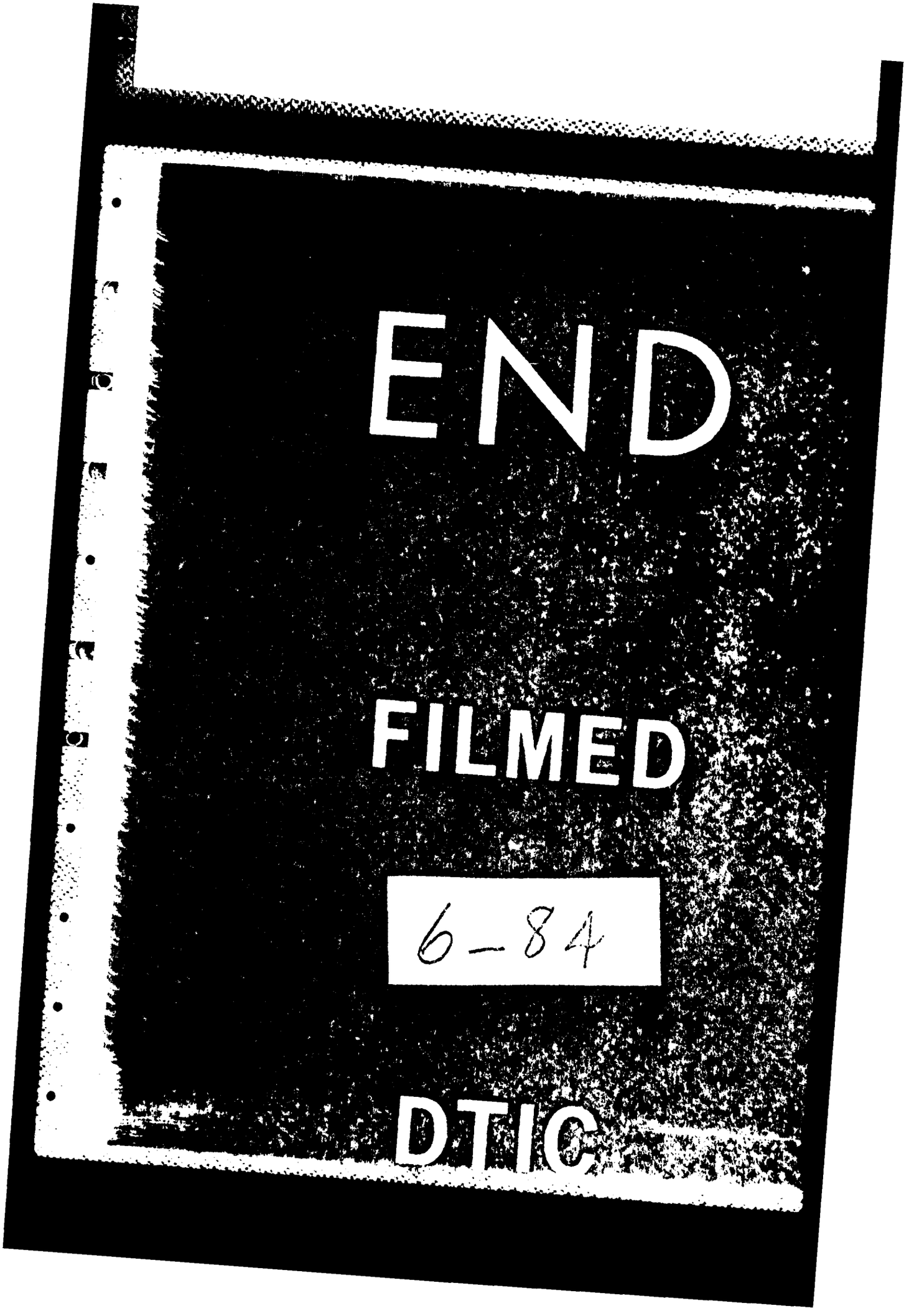
"Light As a Research Tool"

Waynesburg College, Waynesburg, PA, Jan 1982
Hope College, Holland, MI, Feb 1982
Hawaii Section, American Chemical Society, Initiation Banquet, Honolulu, Nov 1982
Science Seminar, Eastern New Mexico State University, Portales, Nov 1982
Boston University, Apr 83
Simmons College, Boston, May 83
Breakthrough Lecture, FLACS Meeting in Miniature, Jacksonville, FL, May 83
Freshmen Chemistry Class, Gonzaga University, Spokane, WA, Oct 83

"Excited States of Transition Metal Complexes: Properties of $(nd)^8$ Monomeric and Dimeric Systems"

ACS Tour Speaker, Southern Arizona Section, Tucson, Feb 1983
Department of Chemistry Seminar, Arizona State University, Tempe, Mar 1983
Purdue University, Apr 83

"Classification of Excited States of Inorganic Complexes", State of the Art Symposium for Chemical Educators VII. Inorganic Photochemistry, 185th National Meeting of the American Chemical Society, Seattle, Mar 1983


END
FILMED
6-84
DTIC